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Contrat n° SPC - 95 - 4015

FINAL REPORT

Title : **Non-Linear Optical Properties of TeX-Derived Glasses**

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	1996	Final Report

4. TITLE AND SUBTITLE	5. FUNDING NUMBERS
Nonlinear Optical Properties of Tex-Derived Glasses	F6170895W0175
6. AUTHOR(S) Prof Jacques Lucas	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Rennes Campus de Beaulieu 35042 Rennes Cedex France	8. PERFORMING ORGANIZATION REPORT NUMBER N/A
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) EOARD PSC 802 BOX 14 FPO 09499-0200	10. SPONSORING/MONITORING AGENCY REPORT NUMBER SPC 95-4015
11. SUPPLEMENTARY NOTES	
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.	12b. DISTRIBUTION CODE A

13. ABSTRACT (Maximum 200 words)

This report results from a contract tasking University of Rennes as follows: The main target of this study was to prepare several new compositions of infra-red glasses, to characterize them with respect to their stability versus crystallization and thermal behavior. These new glasses prepared in a bulk disk shapes have then been investigated by optical measurements in the region of the band gap absorption.

14. SUBJECT TERMS	15. NUMBER OF PAGES
EOARD	25
	16. PRICE CODE N/A

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19, SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. 239-18
298-102

FINAL REPORT

Contrat : SPECIAL PROJECT SPC - 95 - 4015

Between : The University of RENNES
Laboratoire des Verres et Céramiques
Campus de Beaulieu
35042 RENNES, France
Responsible : Professor Jacques Lucas

And : The departement of the Air Force
European office of Aerospace Research and Development
223 old Marylebone road, London NW 1 5TH
Dr O. ELBAYOUMI, Cheef Chemistry

Title of the proposal : **Non-Linear Optical Properties of TeX-Derived Glasses**
Started date May 1995

INTRODUCTION

This research proposal was the result of discussions and cooperations initiated long time ago between two complementary laboratories : 1) the Laboratoire des Verres et Ceramiques at the University of Rennes headed by Professor Jacques Lucas and 2) the Laboratory of Professor Joseph H. Simmons at the Advanced Material Research Center, University of Florida, Gainesville, FL 32611 USA.

The first group is specialized in the development and characterization of new IR glasses, the second laboratory has a recognized expertise in the investigation of the non linear properties of glasses.

OBJECTIVE

The TeX glasses correspond to the acronym covering a large family of IR glasses based on the combination of Tellurium Te , X= Bromine or Iodine , Selenium , Arsenic or Germanium. They are characterized by a large transparency domain covering the two atmospheric IR windows 3 - 5 µm and 8 - 12 µm. Due to a great flexibility in the chemical composition the objective was to control the variation of the band gap absorption and to adjust it in a rather large domain lying from E = 1.5 eV to E = 0.6 eV. The low band gap promises the highest Kerr effect seen in any glass according to the theory of Sheik-Bahae and Van Stryland.

The main target of this study was to prepare several new compositions of infra-red glasses, to characterize them with respect to their stability versus crystallization and thermal behaviour. These new glasses prepared in a bulk disk shapes have then been investigated by optical measurements in the region of the band gap absorption.

THE GLASSES

The Laboratoire des Verres et Céramiques has a long experience in infra-red glasses preparation and characterization. Specially the glasses derived from the original binary Tellurium - Halogen (TeX) systems have been optimized in order to control the glass transition temperature Tg and the resistance towards crystallization and water corrosion. Some totaly new chalcogenides compositions have been also investigated as long as they were leading to glasses with new interesting position of the band gap.

The main feature common to all these glasses is associated with the presence in their structure of chalcogen atoms exhibiting lone pair electronic density. These lone pairs are responsible of the high polarisibility of the atoms and consequently of the potential high non linear properties.

Glass selection

Two families of glasses have been selected for this study. The first one belongs to the Ge-Se-Sb system and the second one, to the TeX glass system.

The preparation of all the glasses was the same. The raw materials are separately purified in order to obtain pure glasses as shown in figure 1 and 2. Tellurium was plunged in a mixture of HBr/Br2 to eliminate the oxides impurities. Selenium and arsenic were respectively heated at 250°C and 350°C under evacuation to eliminate surface oxide impurities. Then, the purified compounds are sealed in a deshydrated silica ampoule under vacuum . The ampoule is heated in a rocking furnace at 600°C for several hours.

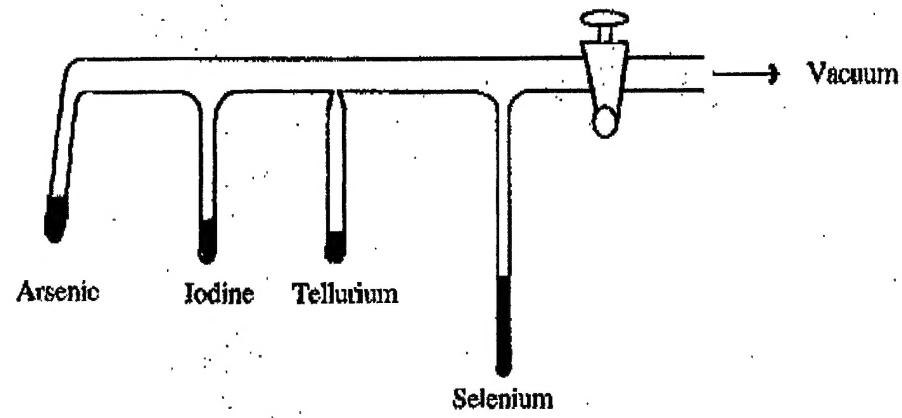


Figure 1: *Apparatus for preparing the TeX glasses containing iodine*

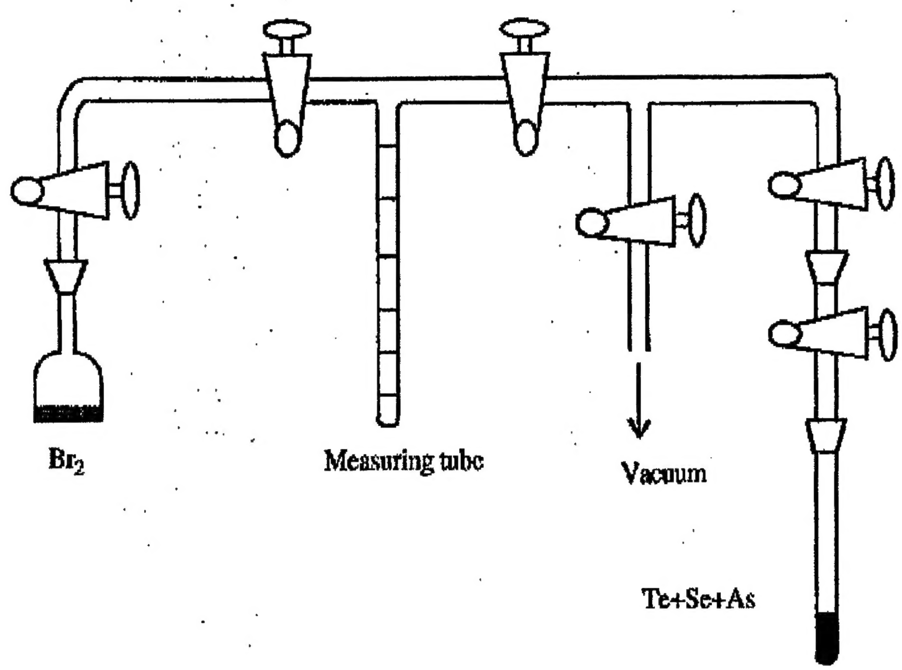


Figure 2: *Apparatus for preparing the TeX glasses containing bromine*

The ampoule is then heated in a rocking furnace at 600°C for several hours. To obtain the core rod, the ampoule was held vertically while cooling to room temperature as shown in figure 3.

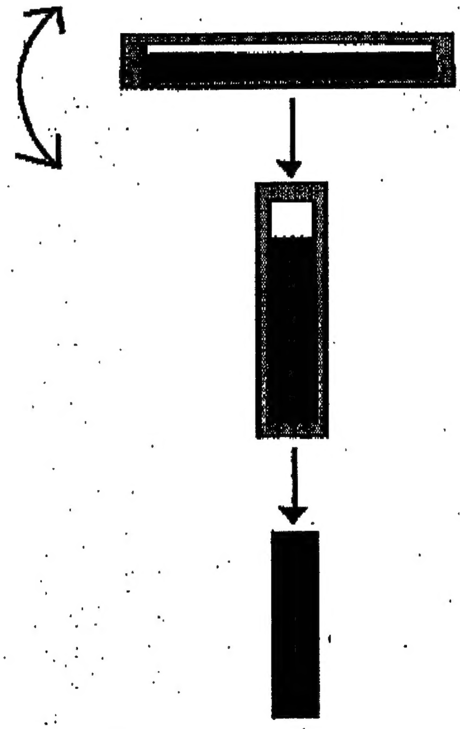


Figure 3: *Method for TeX glass bulk preparation*

The glass transition temperature, Tg, measurements are important to determine if glasses could withstand the service temperature requirement for a particular application.

- The glass 1 has the following composition Ge_2Se_{98}. The Tg equals to 146°C.

- The glass 2 has the following composition $Ge_{20}Se_{80}$ and its Tg equals to 50°C. It is relatively low because of the important quantity of Se.

- The glass 3 has the following composition $Ge_{18}Se_{70}Sb_{12}$ and the Tg equals to 206°C.

- The glass 4 has the following composition $Ge_{30}Se_{60}Sb_{10}$ and a Tg of 292°C.

This family has been investigated because of high Tg.

- The glass 5 has the following composition $Te_2Se_5Br_3$ and a Tg of 84°C wich is relatively low because of the presence of an halogen. This glass is characterized by a 1-D spaghetti structure and transparent in IR from 1 to 20 µm.

- The glass 6 has the following composition $Te_2Se_{3.5}As_4I_{0.5}$ and a Tg = 130°C. Arsenic allows to increase the dimensionality of the glass and also the Tg. This glass has been selected because of its ability to be transformed into IR optical fibers. In this special optical configuration, with a core-clad guiding structure, high optical confinment is possible and efficient non linear properties can be achieved.

- The glass 7 has the following composition $Te_2Se_3As_4Br_1$ and a Tg of 133°C. This glass is interested because of the large IR optical window of fibers in the 7 - 10 µm range.

The TeX family is very interested because of its high resistance against corrosion and crystallization, and also its high facility to realise IR optical fibers.

Optical properties of glasses

The TeX glasses have low phonon energy, making this family of glasses transparent from 1 to 20 microns. The other family based on the Ge-Se-Sb system has been investigated because of its lower band gap energies.

At the University of Rennes, each glass was analysed by IR transmission and the band gap energy λg was calculated for an absorption coefficient $\alpha = 10\ cm^{-1}$. At the University of Florida, Absorbance measures have been realized on the same samples, and the band gap energies λg have been calculated. You will find each transmission and absorbance spectrum in the annexe.

The refraction indice was measured for some TeX glasses and we have estimated another one.

- The glass 1, Ge_2Se_{98}, has a $\lambda g = 0{,}704$ µm. The transparency of this glass goes from 1 to 17 µm. An estimation of the refractive index gives us n = 2.4.

- The glass 2, $Ge_{20}Se_{80}$, has a $\lambda g = 0.738$ µm. The transparency of this glass goes from 1 to 20 µm.

- The glass 3, $Ge_{18}Se_{70}Sb_{12}$ has a $\lambda g = 0.740$ µm. The transparency of this glass goes from 1 to 17 µm.

- The glass 4, $Ge_{30}Se_{60}Sb_{10}$ has a $\lambda g = 0.810$ µm. The transparency of this glas goes from 1 to 17 µm.

- The glass 5, $Te_2Se_5Br_3$, has a $\lambda g = 1.020$ µm. The measured refractive index n = 2.67. The IR optical window goes from 1 to 20 µm.

- The glass 6, $Te_2Se_{3.5}As_4I_{0.5}$, has a $\lambda g = 1.193$ µm. The estimated refractive index n = 2.82. The transparency of this glass goes from 1 to 18 µm.

- The glass 7, $Te_2Se_3As_4Br_1$, has a $\lambda g = 1.248$ µm. The measured refractive index n = 2.87. The transparency of this glass goes from 1 to 18 µm.

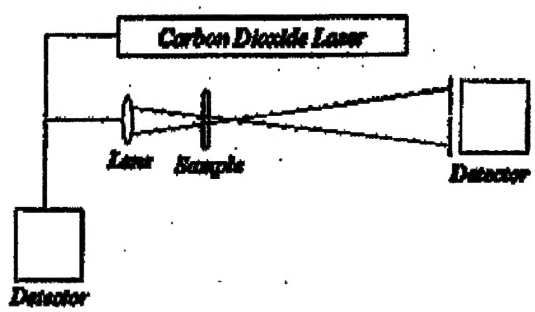
These new chalcogenides glasses resist devitrification and water corrosion. Potential applications in IR optics have been developped. The fibers operating in the 2 - 13 µm range have been tested for remote spectroscopy, CO_2 laser power delivery and pyrometry.

Non-linear optical properties of glasses

The TeX glasses have very low band-edge absorption energies, consequently, they have extremely polarizable valence electron clouds. In addition, due to their large atomic masses, their outer electrons have lower binding energies than oxide glasses. Both these effects combine to suggest a very large non-linear optical (NLO) coefficient, including a very large electronic Kerr Effect.

Current models for NLO models suggest that the electronic Kerr Effect which has a characteristic time in the femtosecond range controls the NLO behavior of glasses at wavelengths longer than twice the absorption edge wavelength of the glass, at which point two-photon absorption begins to dominate NLO behavior. Therefore, in order to measure true Kerr Effect non-linearities, it is necessary to conduct tests at wavelengths many times the absorption edge wavelength.

Tests were conducted at the University of Florida on several TeX glasses, however, data is only currently available on sample 2 with an absorption edge at 0.738μm. The tests were conducted using a carbon dioxide laser with light at 10.6μm, well away from any multi-photon absorption process in this glass. Therefore, the tests measured the true electronic Kerr Effect.



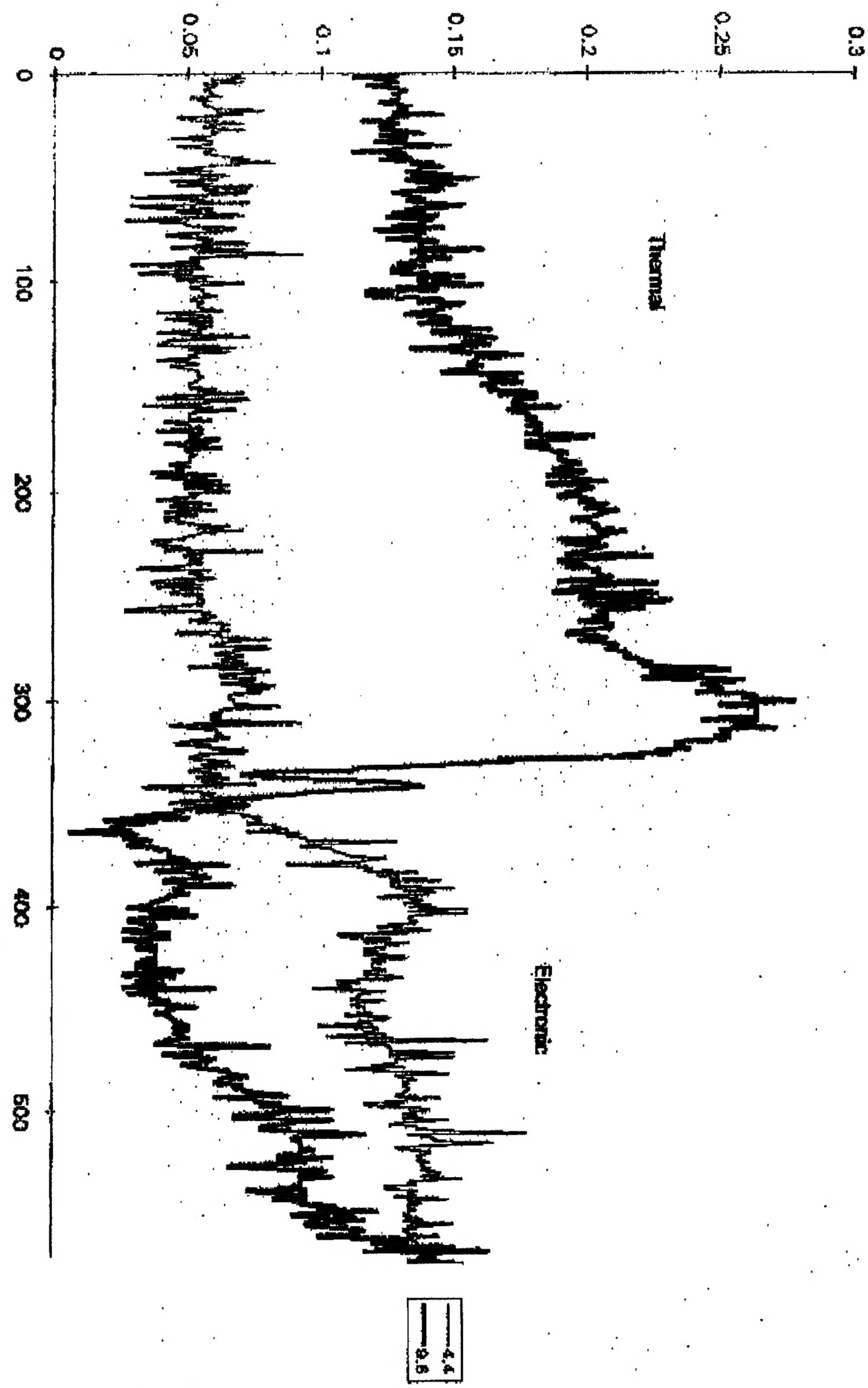
The test set up was designed following the z-scan method of Sheik-Bahae and co-workers [M. Sheik-Bahae, A. A. Said, T. H. Wei, D. J. Hagan and E. W. Van Stryland, IEEE J. Quant. Electronics 26, 760 (1990)]. A diagram of the apparatus is shown. The laser beam is divided into two equal beams, one for reference and the other for the measurement. The light from the second beam is focused by a lens and passes through the sample on its way to an aperture and a detector. As the sample is positioned along the path of the beam, first before the focal point, then past the focal point, the refractive index of the sample will deflect and move the actual focal point, thus increasing or decreasing the intensity of the light at the detector. If the sample has a negative NLO coefficient, it will move the focal point closer to the aperture when located before the focal point and thus increase the intensity. As the sample is moved through the focal point, it will further defocus the beam reducing the intensity. Thus, the intensity difference for a negative NLO material will be positive then negative. By symmetry, the intensity difference for a positive NLO material will be negative then positive. Of course, the electronic Kerr Effect will create a positive NLO coefficient, therefore, one expects that the z-scan data will be negative then positive. Measurements obtained on sample 2 are shown in the attached Figure. It is clear from the data that the electronic Kerr Effect only occurs for the 4.4 watt beam power. At higher powers the observed nonlinearity is negative, indicating that the effect is thermal. In this case, the temperature dependence of the

NLO coefficient is negative.

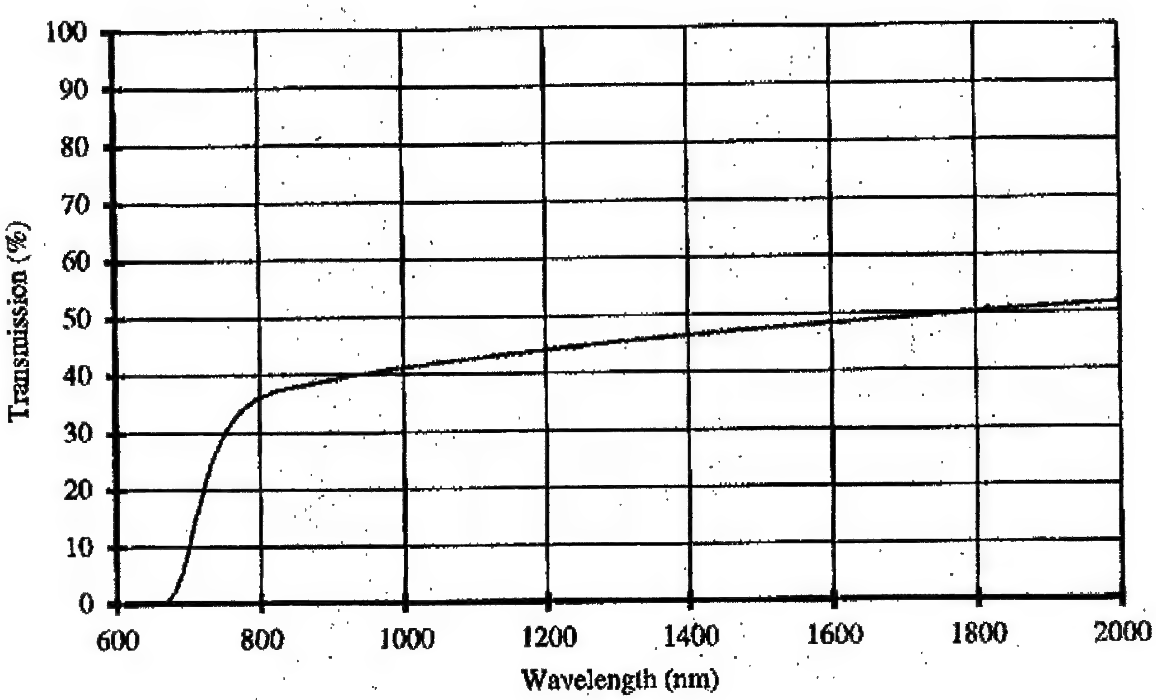
The data can be used to calculate the NLO coefficient of sample 2 from the equation:

$$n_2 = \frac{c\, n_0\, \lambda\, \alpha\, L\, \Delta T_{p\text{-}v}}{32.5\, \pi^2 I_0 (1 - e^{-\alpha L})} \quad esu$$

where c = speed of light in vacuum, n_0 = linear refractive index, and $\Delta T_{p\text{-}v}$ is the maximum change in intensity in going across the focal point. The intensity term in the denominator when applied to TeX glasses must also take into account the large reflectivity coefficients demonstrated by these materials. A preliminary calculation yields a NLO coefficient of about 1×10^{-6} esu which is 100,000 times larger than CS_2 or the highest measured lead-bismuth-gallate glass to date. When considering the Two-photon-Absorption model of Sheik-Bahae and co-workers, which shows that the Kerr NLO coefficient will scale in the order of the bandgap energy to the 4th power, we compare the lead-bismuth gallate glasses with absorption edges at 470 nm with sample 2 having an edge at 738 nm, the model only predicts an improvement of a factor of 6 instead of the large figure obtained here. Consequently, other mechanisms are contributing to the added nonlinearity, including the non-oxide anion. This process is under further investigation, as is the thermal contribution. Other TeX glasses will be studied.

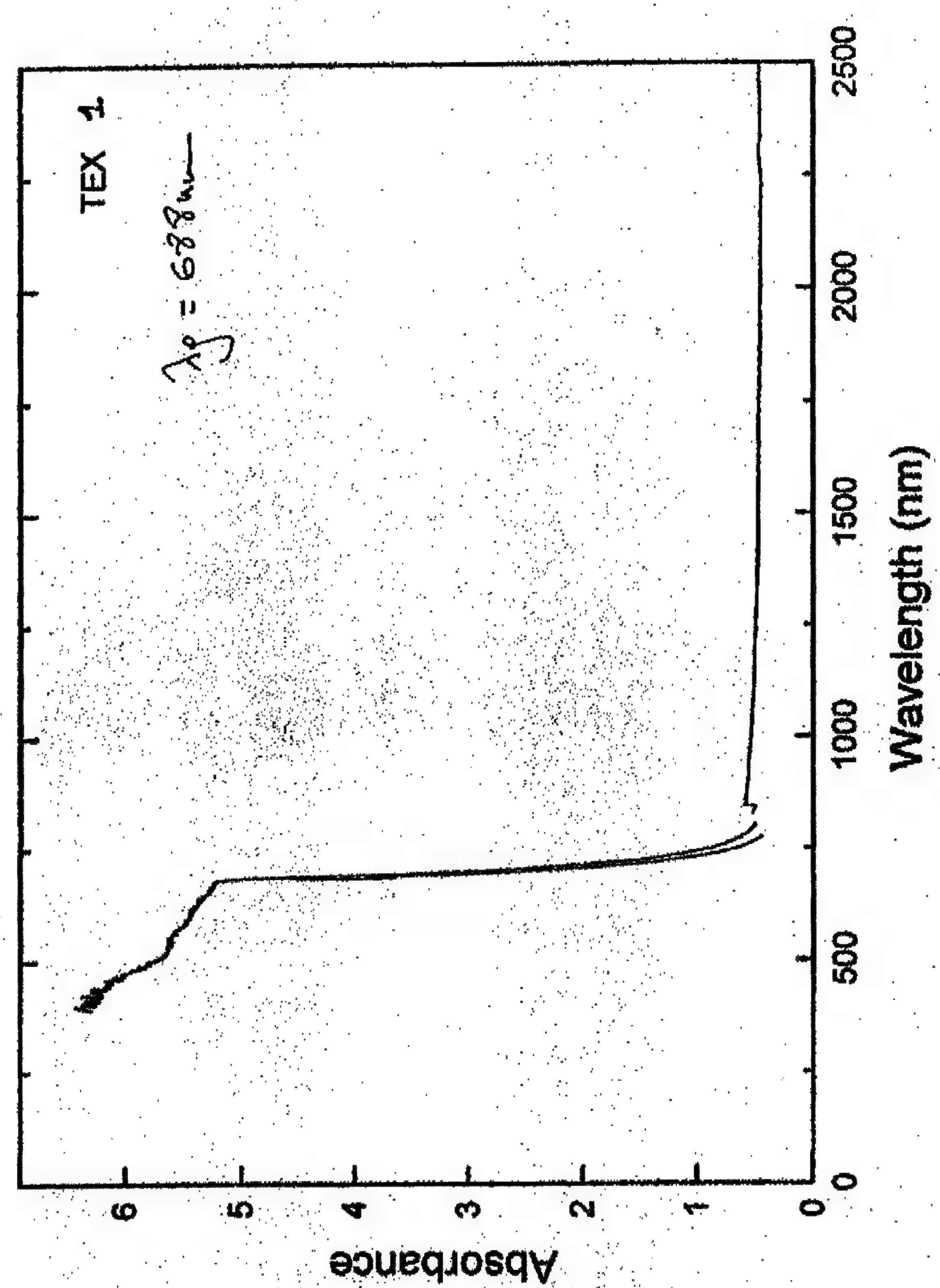

0
0.05
0.1
0.15
0.2
0.25
0.3
0
100
200
300
400
500
Thermal
Electronic
4.4
9.8

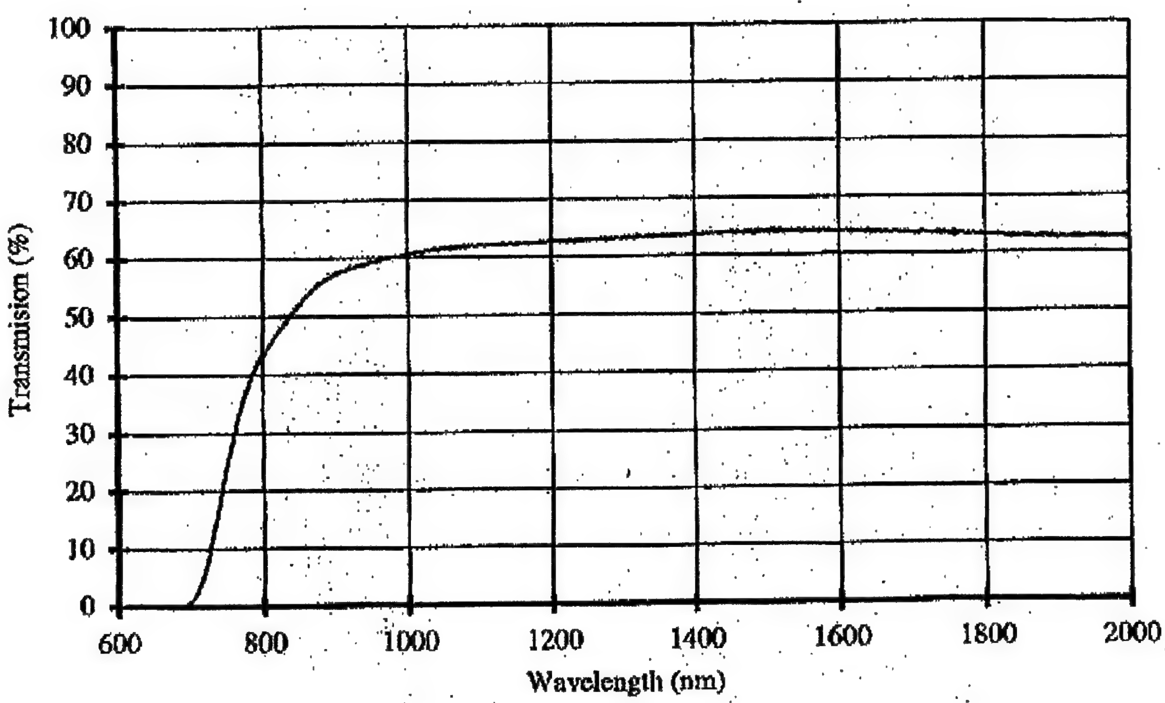
ENCLOSURES



Glass composition : Ge_2Se_{98}

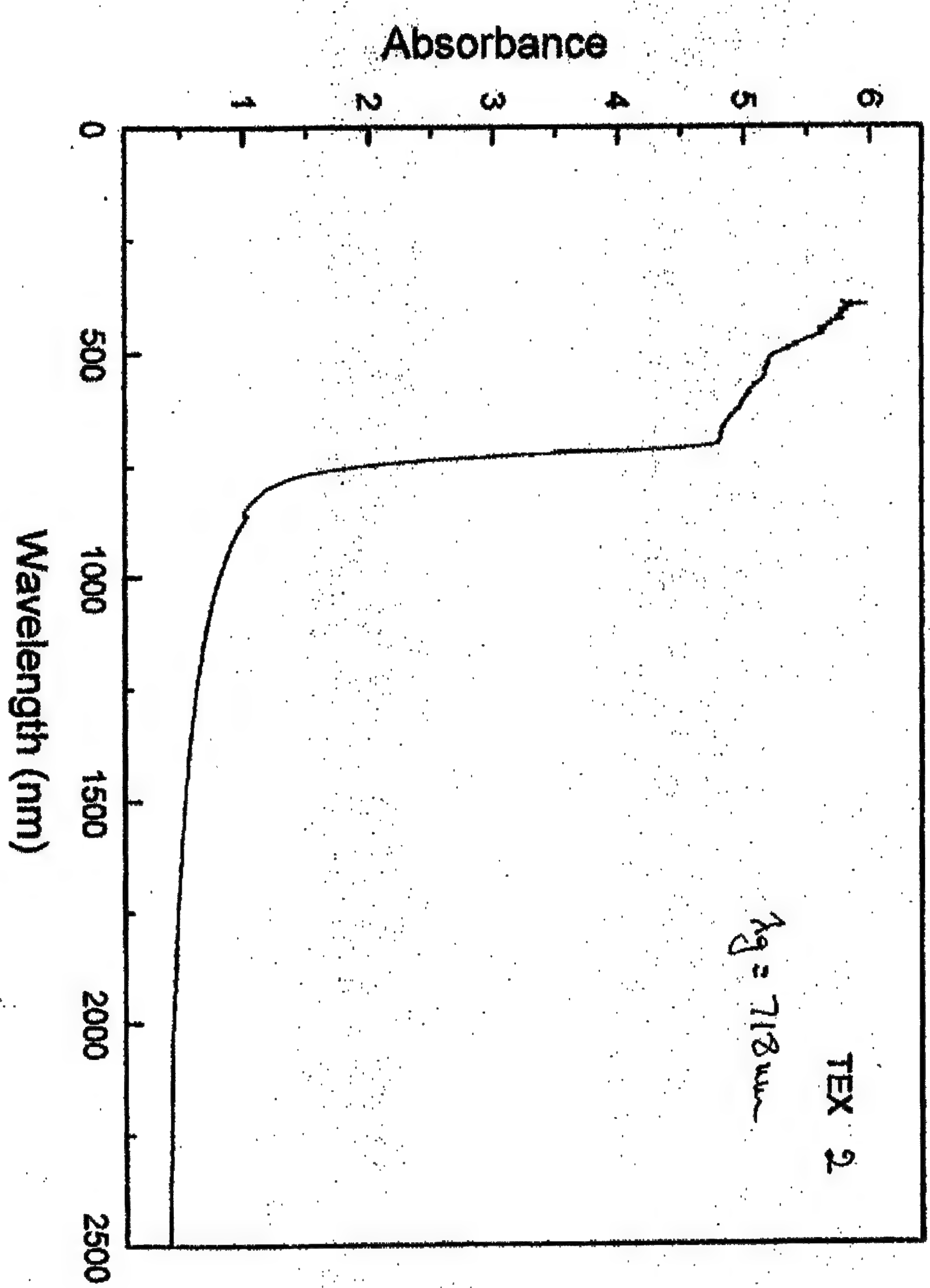
λ_g = 0,704 µm

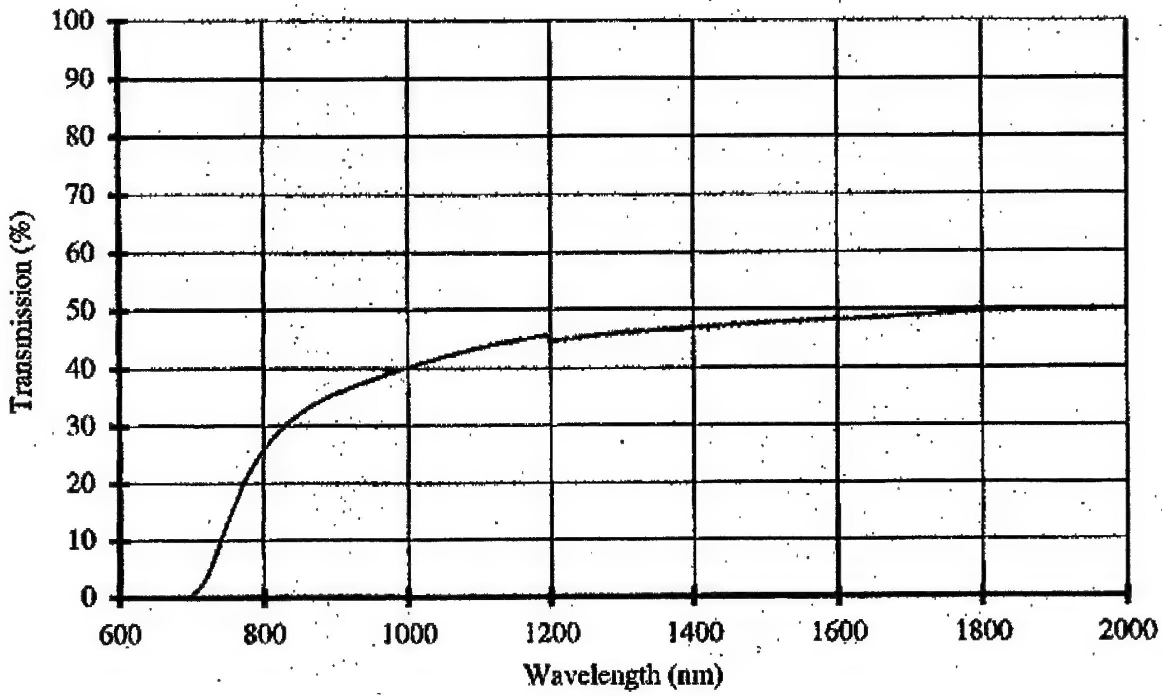

TEX 1
Absorbance
Wavelength (nm)
0
1
2
3
4
5
6
0
500
1000
1500
2000
2500



Glass composition : $Ge_{20}Se_{80}$

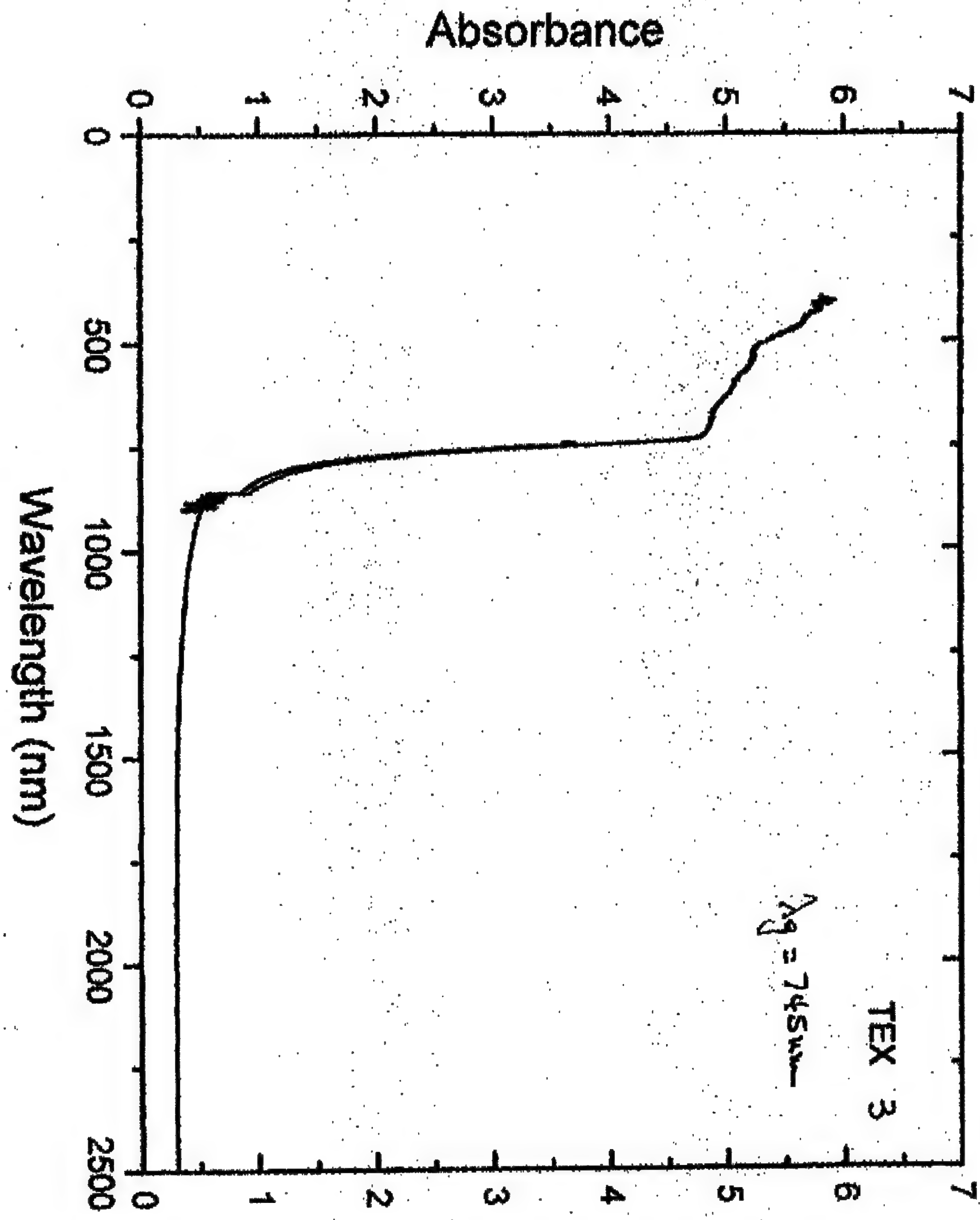
$\lambda_g = 0{,}738$ µm

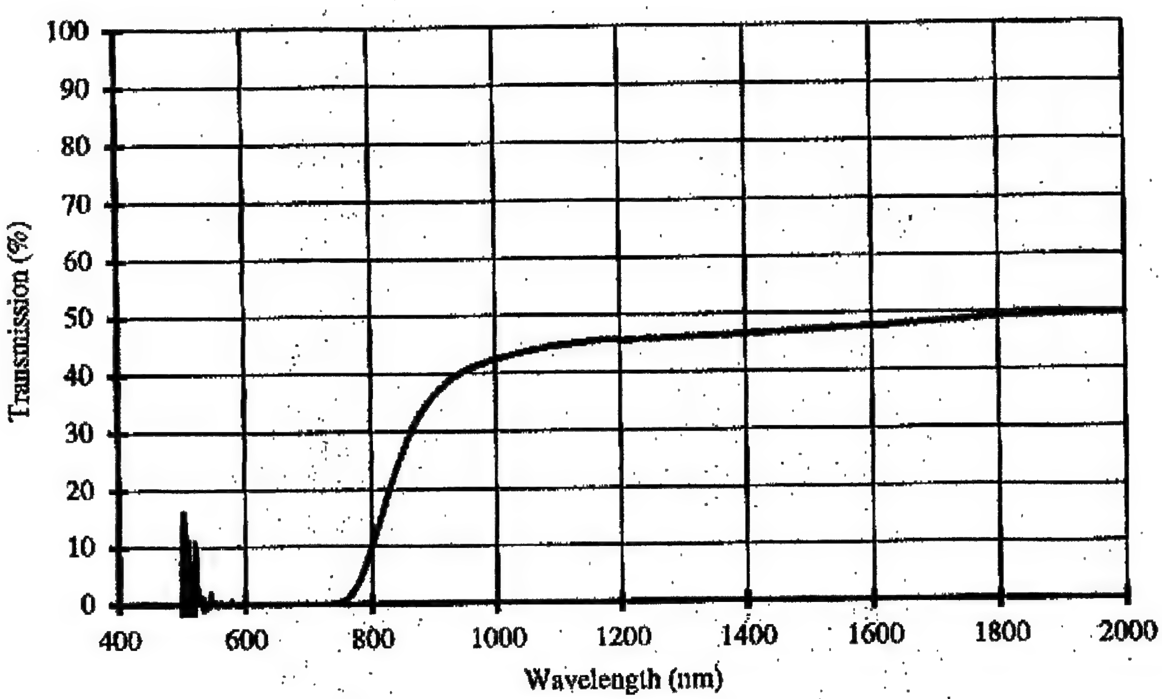

Absorbance
1
2
3
4
5
6
0
500
1000
1500
2000
2500
Wavelength (nm)
TEX 2



Glass composition : $Ge_{18}Se_{70}Sb_{12}$

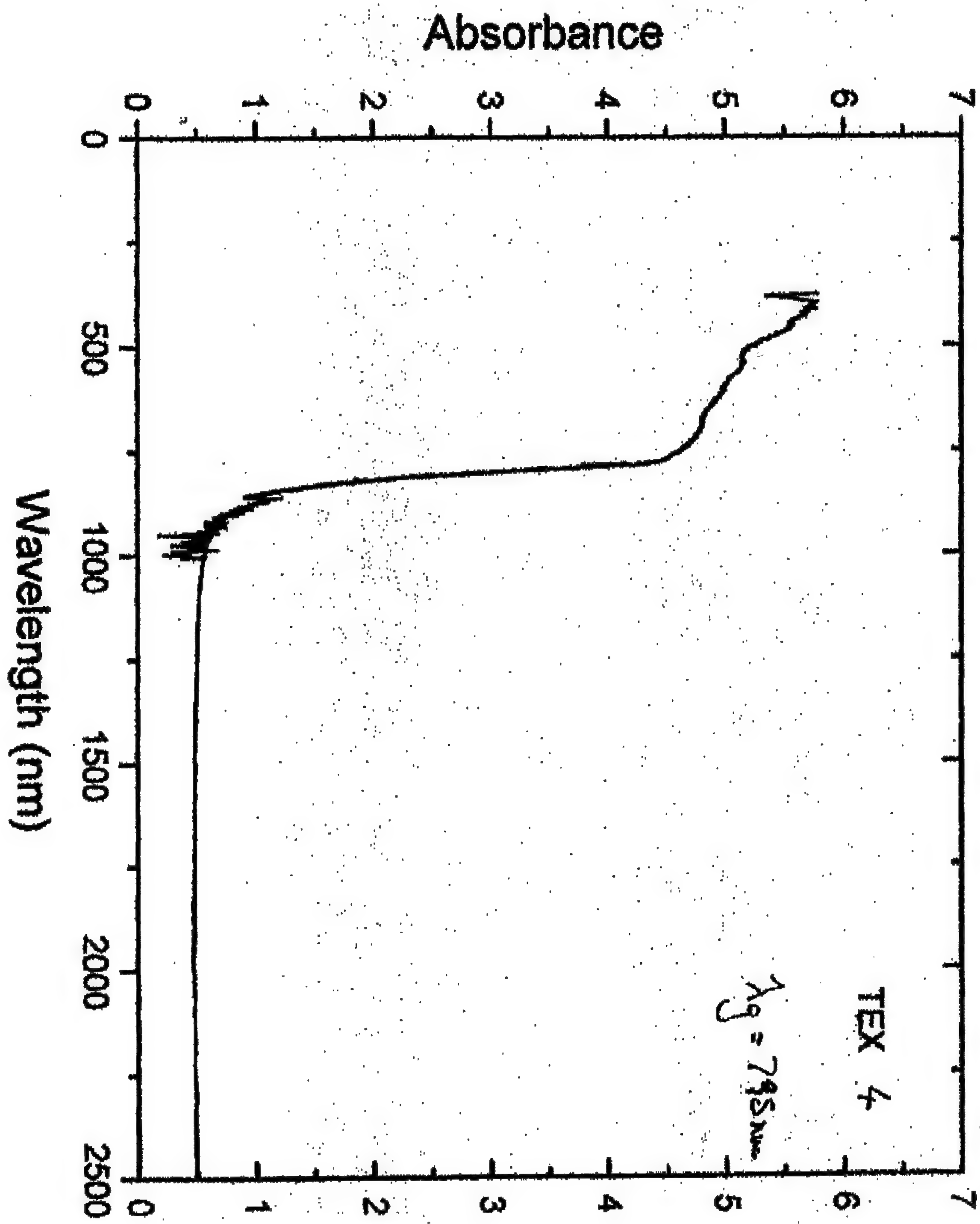
$\lambda_g = 0{,}740\ \mu m$

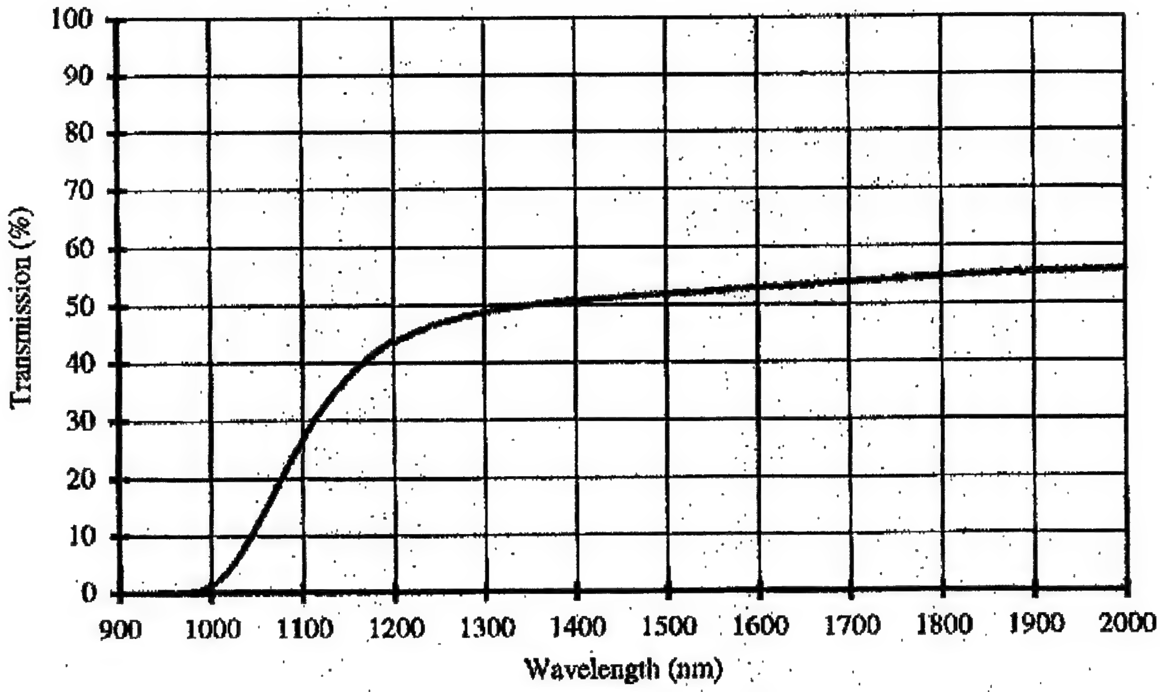

Absorbance
0 1 2 3 4 5 6 7
Wavelength (nm)
0 500 1000 1500 2000 2500
TEX 3
λg = 745nm



Glass composition : $Ge_{30}Se_{60}Sb_{10}$

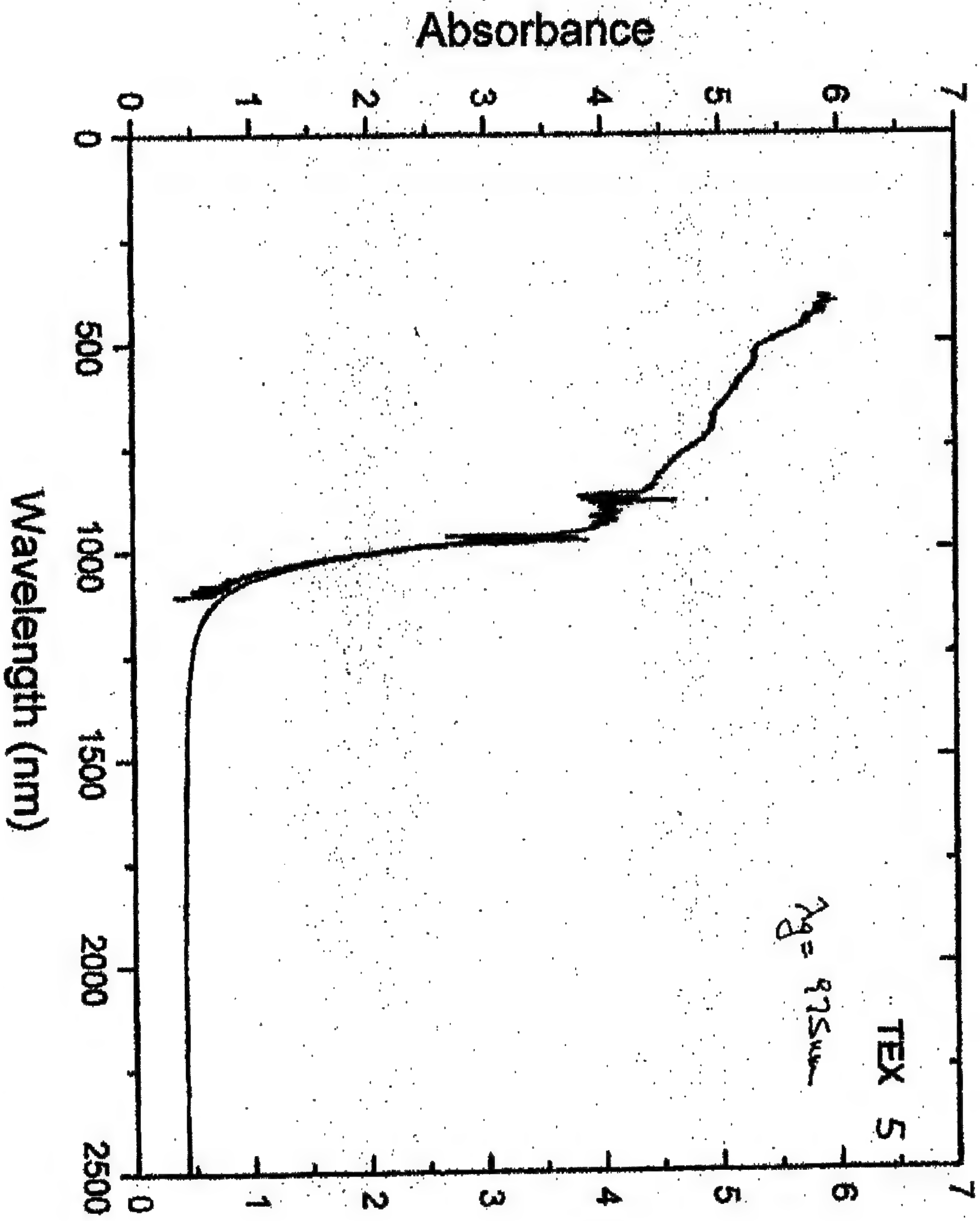
$\lambda_g = 0{,}810\ \mu m$

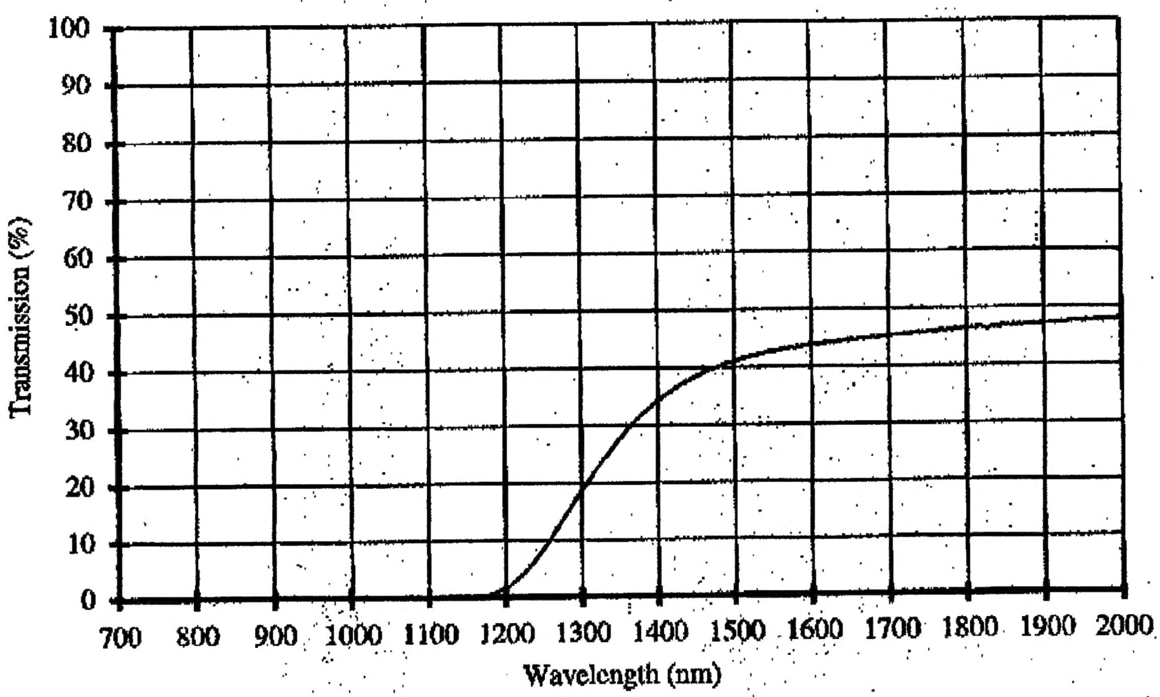

Absorbance
0
1
2
3
4
5
6
7
0
500
1000
1500
2000
2500
Wavelength (nm)
TEX 4
λg = 795nm



Glass composition : $Te_2Se_5Br_3$

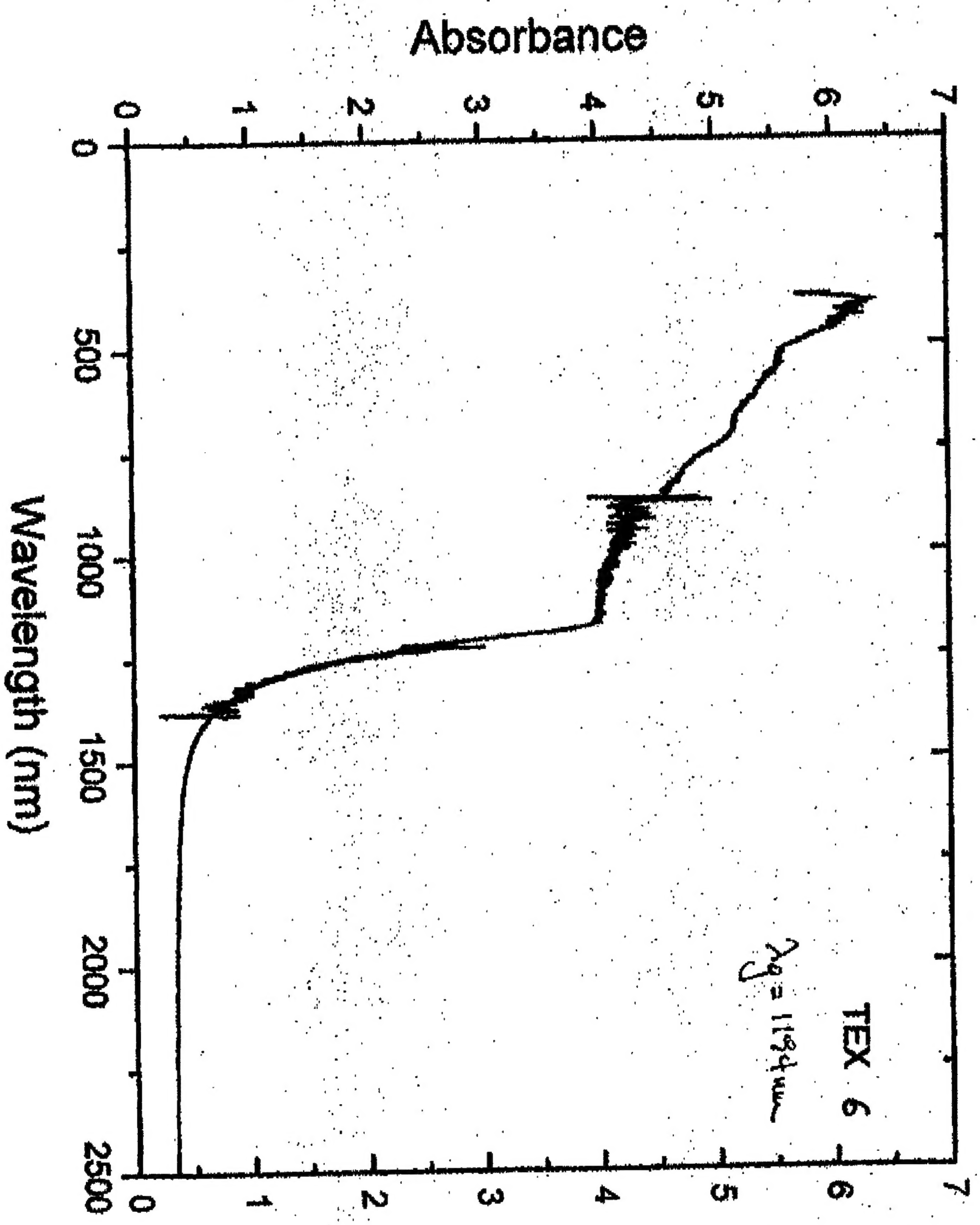
λ_g = 1,020 µm

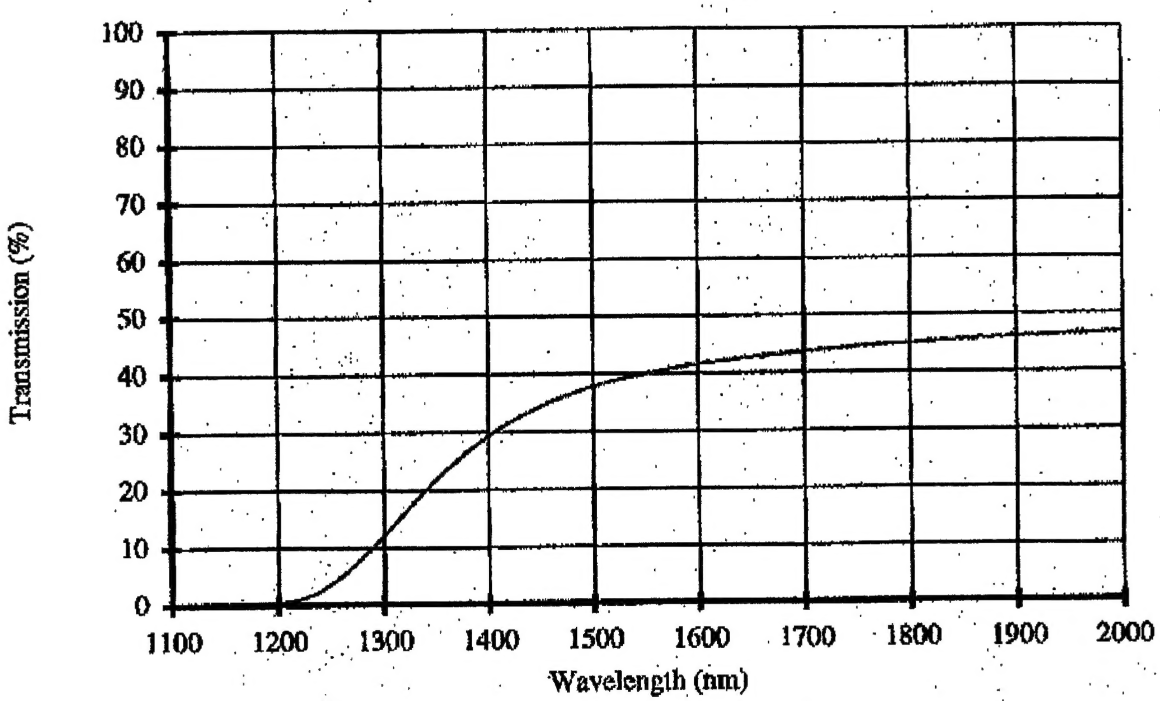

Absorbance
Wavelength (nm)
TEX 5
λg = 975nm
0
1
2
3
4
5
6
7
0
500
1000
1500
2000
2500



Glass composition : $Te_2Se_{3,5}As_4I_{0,5}$

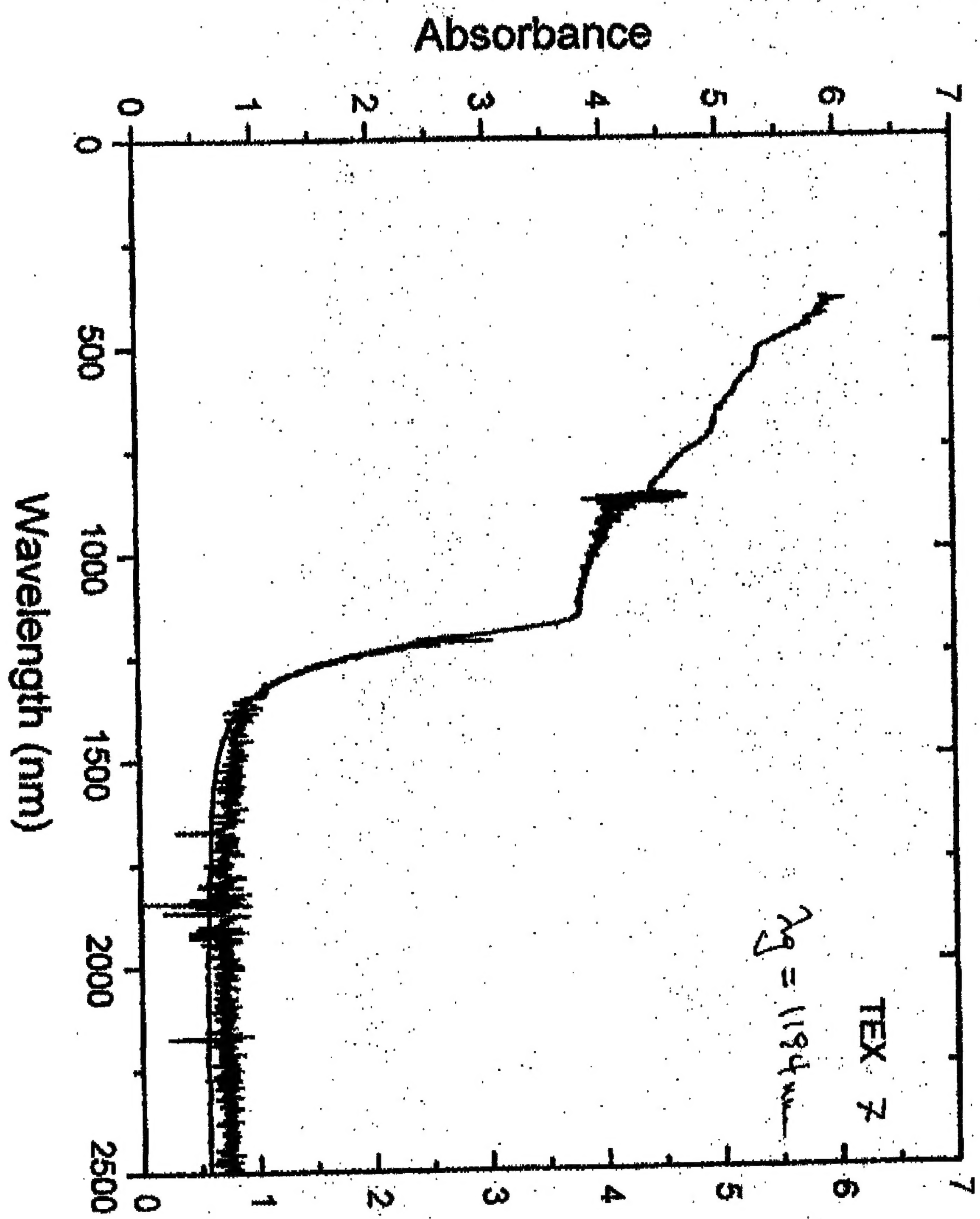
$\lambda_g = 1{,}193\ \mu m$


Absorbance
0
1
2
3
4
5
6
7
Wavelength (nm)
0
500
1000
1500
2000
2500
TEX 6
λg = 1194nm



Glass composition : $Te_2Se_3As_4Br_1$

$\lambda_g = 1{,}248\ \mu m$


Absorbance
Wavelength (nm)
TEX 7
λg = 1194 nm
0
500
1000
1500
2000
2500
0
1
2
3
4
5
6
7